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The Efficacy of Certain Substituted Phenols and their Salts as Fungicidal Agents

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The *Butler University Botanical Studies* journal was published by the Botany Department of Butler University, Indianapolis, Indiana, from 1929 to 1964. The scientific journal featured original papers primarily on plant ecology, taxonomy, and microbiology. The papers contain valuable historical studies, especially floristic surveys that document Indiana's vegetation in past decades. Authors were Butler faculty, current and former master's degree students and undergraduates, and other Indiana botanists. The journal was started by Stanley Cain, noted conservation biologist, and edited through most of its years of production by Ray C. Friesner, Butler's first botanist and founder of the department in 1919. The journal was distributed to learned societies and libraries through exchange.

During the years of the journal's publication, the Butler University Botany Department had an active program of research and student training. 201 bachelor's degrees and 75 master's degrees in Botany were conferred during this period. Thirty-five of these graduates went on to earn doctorates at other institutions.

The Botany Department attracted many notable faculty members and students. Distinguished faculty, in addition to Cain and Friesner , included John E. Potzger, a forest ecologist and palynologist, Willard Nelson Clute, co-founder of the American Fern Society, Marion T. Hall, former director of the Morton Arboretum, C. Mervin Palmer, Rex Webster, and John Pelton. Some of the former undergraduate and master's students who made active contributions to the fields of botany and ecology include Dwight. W. Billings, Fay Kenoyer Daily, William A. Daily, Rexford Daudenmire, Francis Hueber, Frank McCormick, Scott McCoy, Robert Petty, Potzger, Helene Starcs, and Theodore Sperry. Cain, Daubenmire, Potzger, and Billings served as Presidents of the Ecological Society of America.

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THE EFFICACY OF CERTAIN SUBSTITUTED PHENOLS AND THEIR SALTS AS FUNGICIDAL AGENTS[1]

By Gene M. Le Fave[2] and Bruce L. Skiles

Amine addition products of polychlorophenols have formed the subject of a large number of patents but have not been exploited to any extent as fungicides of commerce.

We have prepared a series of various amine salts of polychlorophenols utilizing, for the most part, pentachlorophenol. The majority of the compounds prepared are new although a few have appeared in the patent literature (1). A few copper compounds were also prepared along with some interesting miscellaneous phenolics. The more promising materials were selected and evaluated for their mildew-proofing properties in textiles by the fungus mat method (2) and in paint by the recently developed accelerated method of Vicklund, *et al* (3).

PREPARATION AND PROPERTIES OF THE AMINE PENTACHLOROPHENATES

Pure pentachlorophenol was obtained by an efficient steam distillation of the technical product and recrystallization from carbon tetrachloride. Other phenols used were obtained commercially in a stated purity of 98% or higher. The amines were obtained with a minimum purity of 98% or were purified to that extent. The fatty amines were supplied gratuitously by Dr. L. Armstrong of the Armour Company and used without further purification.

The majority of the compounds were prepared simply by warming a molecular equivalent each of the amine and phenol in a mutual solvent such as methanol and allowing the product to crystallize or

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[1] Presented before the Pesticide Seetion of the XIIth International Congress of Pure and Applied Chemistry, Paper No. 18, September 12, 1951. A considerable amount of the evaluation work represents a portion of a thesis submitted by Mr. Skiles in partial fulfillment of the requirements for the Master of Science degree in the Division of Graduate Instruetion, Butler University.

[2] J. I. Holcomb Research Laboratories, Indianapolis 8, Indiana.

stripping the solvent if a liquid. An alternative method was occasionally employed; aqueous solutions of the amine hydrochloride and sodium phenate were mixed, precipitating the amine phenate metathetically.

Of the amine polychlorophenates prepared the majority are white crystalline solids although some are heavy oils. They are freely soluble in most organic solvents and relatively insoluble in water. Some, such as the pyridine, acridine and nicotine addition products appear to be molecular complexes resembling hydrocarbon picrates rather than true salts. These complexes, like the picrates, are quite stable.

FUNGICIDAL EVALUATION

All compounds were screened initially against *Alternaria solani* by the modified spore-germination method of Peterson (4), the results of which were found to be reproducible within an error of five per cent at a spore concentration of 5 x 10^4 / ml.

Results of the screening tests appear in Tables I, II, III, and IV. We believe, that considering the limitations imposed by the genestatic approach to laboratory assay of fungicides, the results are reliable. Subsequent mildew-proofing tests employing the fungicides found superior by the Peterson method support this view in part. The reliability would obviously be vitiated upon variation of fungus species and chemical type of fungicide.

It is apparent from the screening data that the fatty amine addition products of the chlorinated phenols are quite superior as fungicides toward sporulating fungi. The highest range of activity lies between ten and sixteen carbon atoms. The lower molecular weight amine salts in general appear to be equal or inferior to pentachlorophenol alone. Branching of the straight chain aliphatic amines reduces the potency of the salt.

An explanation of the high order of activity of the fatty amine salts of the substituted phenols may be found in the fatty amines themselves. They were found to possess an exceptionally high antifungal activity which will comprise the subject of a future report to be published elsewhere.

It is of passing interest to note that the majority of the amine pentachlorophenates, on the basis of their infra-red patterns in the hydrogen-bond region, show almost complete dissociation.

We find it rather difficult to account for the activity of the aminopropionitrile salts since the aminopropionitriles possess no fungicidal activity whatever. Perhaps a synergistic action is involved. Indeed, synergism is operative in a large number of the amine salts when the proportional molecular weight contribution of the phenolic moity is considered.

EVALUATION OF SELECTED COMPOUNDS AS MILDEW-PROTECTANTS FOR PAINT

By modifying the method of Vicklund and his co-workers (3) slightly it proved entirely satisfactory for our purposes. The aggressive growth characteristics of the organisms used, i.e., *Aspergillus niger, Aspergillus oryzae* 458 and 692, and the simulated tropical environment made it necessary to use a quantity of toxicant amounting to two per cent based on the weight of the paint. Less than this proportion allowed for little differentiation in the amount of growth.

Our observations indicate the following order of effectiveness:

> Copper-8-hydroxyquinolate >> n-Decylamine pentachlorophenate > n-Hexadecylamine pentachlorophenate > "Cocoamine" pentachlorophenate > N-Butyl-*o*-hydroxybenzylimine, copper salt > b, b'-iminodipropionitrile pentachlorophenate > pentachlorophenol > Di-beta-naphthol > butylamine pentachlorophenate.

The characteristic inhibitive properties of most copper compounds appear to operate very efficiently in paint with respect to phenolic compounds. This is in agreement with the findings of Vicklund who used *Aspergilli* as test organisms (3).

EVALUATION OF SELECTED COMPOUNDS FOR MILDEW-PROOFING OF TEXTILES

In Table V are listed the results of mildew-proofing tests carried out against *Chaetomium globosum* according to Marsh and Greathouse (2). The fabric strips were so treated so as to retain 1 ± 0.05% of their weight of toxicant. The breaking strength represents an average of three strips. The results are in relatively good agreement with what could be expected from the screening data.

SUMMARY

1. A group of amine polychlorophenates were prepared and screened by Peterson's modified spore germination method against *Alternaria solani.*

2. The more promising of these addition products were further screened against other organisms and evaluated as mildew-protectants for paint and textile.

3. The fatty amine pentachlorophenates were found to be very effective mildew-proofing agents on the basis of limited tests.

4. Several miscellaneous copper and phenolic compounds were prepared and screened.

ACKNOWLEDGMENT

We wish to express our appreciation to Dr. Rex Webster for his many helpful suggestions.

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TABLE I

Fungicidal Activity of Amine Pentachlorophenates in Per Cent Germination of *Alternaria Solani* Spores

Amine Salts	Concentration in Weight Per Cent		
	1.0	0.1	0.01
Pentachlorophenol	0	0	90
Butylamine	0	0	93
1,1,3,3-Tetramethylbutylamine	1	17	
Triethylamine	0	8	
Decylamine	0	0	2
Hexadecylamine	0	0	8

TABLE I—(Continued)

Fungicidal Activity of Amine Pentachlorophenates in Per Cent Germination of *Alternaria Solani* Spores

Amine Salts	Concentration in Weight Per Cent 1.0	0.1	0.01
Octadecylamine	2	10	74
3,5,5-Trimethylhexylamine	3	18	
Isopropylamine	0	2	89
Ethylamine	0	0	90
Octylamine	15	65	
Dodecylamine	0	0	2
Tetradecylamine	0	0	13
Morpholine	0	0	89
N-Methylmorpholine	0	0	90
Ethanolamine	0	0	92
Diethanolamine	3	54	
Triethanolamine	0	14	
Tetraethanolammonium	7	53	
Hexamethylenetetramine (Mono)	0	16	80
Pyridine	0	70	
Acridine	13	32	
Nicotine	2	6	71
Triamylamine	0	22	
Phenylhydrazine	6	19	
Thialdine	2	25	
β, β'—Iminodipropionitrile	0	2	8
β-Dimethylaminopropionitrile	0	0	5
β-Isopropylaminopropionitrile	0	0	17
Di-(2-Ethylhexyl)amine	30	74	
N-Methyltaurine	6	20	

TABLE II

Fungicidal Activity of Mixed Amine Polychlorophenates in Per Cent Germination of *Alternaria Solani* Spores

Amine Salts	Concentration in Weight Per Cent 1.0	0.1	0.01
"Cocoamine"[a] Pentachlorophenate (From Coconut Oil)	0	4	22
"Cocoamine" 2,6-Dichloro-4-Nitrophenate	22	40	
"Cocoamine 2,4,6-Trichlorophenate	1	15	86
"Cocoamine" 2,4,5-Trichlorophenate	11	27	
"Cocoamine" Tetrachlorophenate	1	8	45
"Rosin Amine D"[b] Pentachlorophenate	0	7	59
"Sec.-Cocoamine"[a] Pentachlorophenate	26	69	

TABLE II—(Continued)

Fungicidal Activity of Mixed Amine Polychlorophenates in Per Cent Germination of *Alternaria Solani* Spores

Amine Salts	Concentration in Weight Per Cent 1.0	0.1	0.01
"Amine 2HT"[a] Pentachlorophenate (Sec. C_{16} & C_{18} Amines)	17	96	
"Amine TO"[a] Pentachlorophenate (Rosin & Fatty Amine Mixture)	0	1	89
"Alkylamine 81"[c] Pentachlorophenate Tert., Branched, Primary C_{12} to C_{15})	0	45	
"Alkylamine JM"[c] Pentachlorophenate (Tert., Branched, Primary C_{18} Av.)	0	0	31

(a) Armour & Company.
(b) Hercules Powder Co.
(c) Rohm & Haas Company.

TABLE III

Fungicidal Activity of Some Miscellaneous Compounds in Per Cent Germination of *Alternaria Solani* Spores

Compound	Concentration in Weight Per Cent 1.0	0.1	0.01	0.001
Copper-8-Quinolinolate	3	8	15	24
Copper-N-Methyltauride	0	4	97	
Copper-N-Methyltauro-pentachlorophenate	0	9	46	
Copper-2-Mercapto-phenylthiourea	0	10	68	
Undecylenic Acid	0	0	0	96
m-Hydroxybenzotrifluoride	0	0	100	
β-Naphthol	0	0	91	
β-Di-Naphthol	0	0	24	
Hexachlorophene (G-11)	0	3	7	35
N-Butyl-o-Hydroxybenzolimine	93	100		
Copper Salt	0	23	96	
o-Tydroxyphenylbenzothiazole, Copper Salt	0	0	94	
o-Hydroxyphenylbenzothiazole	11	25		
o-Hydrozyphenylbenzoxazole	2	30	100	
Copper Salt	0	63		

TABLE IV

Maximal Concentration Ranges of Certain Amine Pentachlorophenates Required to Inhibit Germination of 50 Per Cent of Spores

Amine Salts	Organism				
	Aspergillus niger	*Rhizopus nigricans*	*Glomerella cingulata*	*Sclerotinia fructicola*	*Stemphylium sarcineforme*
Pentachlorophenol	0.1-0.01	0.1-0.01	0.01-0.001	0.01-0.001	0.1-0.01
Decylamine Pentachlorophenate	0.01-0.001	0.01-0.001			
Ethanolamine Pentachlorophenate	0.1-0.01	0.01-0.001			
"Cocoamine" Pentachlorophenate	0.01-0.001	0.01-0.001	0.01-0.001	0.01-0.001	0.01-0.001
β, β'-Iminodipropionitrile Pentachlorophenate	0.1-0.01				

TABLE V

The Efficacy of Selected Amine Pentachlorophenates as Textile Mildew-Proofing Against *Chaetonomium globosum*

Compound	Per Cent Residual Strength	Per Cent Residual Strength After 24 Hours Leach at 30° C
Pentachlorophenol	90	30
Decylamine Pentachlorophenate	93	76
Hexadecylamine Pentachlorophenate	91	51
"Rosin Amine D" Pentachlorophenate	86	35
"Cocoamine" Pentachlorophenate	83	54
"Amine TO" Pentachlorophenate	87	30
β, β'-Iminodipropionitrile Pentachlorophenate	95	30